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The structure of a DMSO/Water mixture from Car–Parrinello simulations

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The mixture of DMSO–water was studied with Car–Parrinello simulation techniques. A three-fold coordination at the DMSO oxygen, methyl group hydrogen–oxygen atom contacts, Rüssel-structures and 1-DMSO–3-H_2O clusters are observed. The H(DMSO)–O(H_2O) and the H(DMSO)–H(H_2O) radial distribution functions are almost identical. For different far water the angular distribution displays a dialectic character: Close water orient with the oxygens to the methyl hydrogen far waters vice versa. The emerging picture for the dynamical behavior of the methyl groups is that of a *near-hydrophilic–far-hydrophobic*, where the hydrophobic character is probably dominant. A detailed mechanism of one such an event is given.

1. Introduction

Many experimental quantities of the DMSO–water mixture expose a non-additive behavior [1] mostly at n_{DMSO}=0.2–0.3. The special features of the phase diagram in this region led to the believe that 1-DMSO–3-H_2O and 1-DMSO–2-H_2O clusters would be responsible [1]. In order to find an explanation molecular dynamics simulations based on classical pair potentials were undertaken [2–9]. These studies elucidated cluster of the 1-DMSO–2-H_2O and 2-DMSO–1-H_2O type but no 1-DMSO–3-H_2O cluster were found. The absence of such a 1-DMSO–3-H_2O cluster has prompted this study of the n_{DMSO}=0.25 system with the Car–Parrinello simulation technique. The Car–Parrinello method has the advantage of calculating the intermolecular forces on the fly, i.e. no pre-made interaction model is involved. Polarization effects are explicitly included and the pairwise additivity as used in the traditional molecular dynamics simulations is circumvented. Previous static calculations of different clusters indicated many-body effects up to 30% [10]. Influences of the approximations made in the previous molecular dynamics simulation on calculated quantities were first systematically studied by Huber [11] with models obtained from *ab initio* quantum chemical calculations.

The aim of this study is to reveal the structure of the DMSO–water mixture in order to help to understand the non-additive behavior of this system.

2. Methodology

The simulation was undertaken employing a Car–Parrinello [12] ansatz, where the electronic structure was calculated within the Kohn–Sham formulation of density functional theory (DFT) in combination with the BLYP functional [13,14]. In order to investigate the performance of BLYP few static calculations with TURBOMOLE [15] and the TZVP basis on the $(H_2O)_2$, the $(DMSO)_2$ and the DMSO–water dimer are given in table 1. B3LYP and MP2 data are from [10]. Only for the DMSO-dimer energy a considerable deviation of the BLYP results from the other methods is found. For the water and DMSO/water systems a good agreement between all methods is observed, with BLYP showing the lowest interaction energy in all cases.

The combination of DFT(BLYP) with dynamic

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Table 1
Dimer interaction energies in kJ/mol.

cluster	BLYP	B3LYP	MP2
$(H_2O)_2$	−18.5	−19.9	−18.0
$(DMSO)_2$	−27.8	−35.8	−41.6
H_2O–DMSO	−35.3	−40.0	−37.5

simulations allows different perspectives than the simulations with empirical model potential utilizing an united atom ansatz and pairwise additivity. The strength of the DFT based simulations lies in the fact that all molecules are fully flexible (in contrast to the united atom ansatz) and the circumvention of the pairwise additivity. Furthermore, no interaction models are involved where the system is fitted to a certain condition of pressure or temperature and the electronic structure is available all the time.

The plane wave basis is expanded up to a cutoff of 70 Ryd. Atomic pseudopotentials of Troullier and Martins [16,17] treated the inner core electrons. The calculations were performed with the CPMD code [18]. 32 molecules at a composition of n_{DMSO}=0.25, i.e. 8 DMSO and 24 water (152 atoms) in a box of size 14 Å with periodic boundary conditions were used. 14 Å follows from the experimental density at standard condition 18138.6 mol· m^3. Note, the size of the system is not sufficient enough to describe all solvation shells. It is known from diffraction data, that the maximum radius for which the pair correlation functions is reliably derived in this system is of the order of 10 Å. This requires a minimum box size of 20 Å [19], which would mean a system of 88 molecules, i.e. 22 DMSOs and 66 H_2Os (418 atoms). However, we are mainly interested in the short-range behavior of the methyl groups. This behavior will most likely not significantly change by increasing the size of the system. To allow for a bigger time step (0.145 fs) the mass of deuterium was chosen for all hydrogens. The system was first equilibrated with traditional molecular dynamics simulations using the setup of [5] for several 100 ps, because this calculations are very cheap. Next we changes to the Car-Parrinello simulation and enforced a temperature of 600 K for a few ps. After equilibrating at a temperature of 300 K for several ps, we run a separate trajectory for 9.5 ps in a microcanonical ensemble.

To analyze the structure radial distribution functions g(r) were calculated from normalized histograms of the distances between the various atom pairs. Angular distributions were calculated to elucidate the orientation of the molecules.

3. Microscopic pictures

The first insight into the microscopic structure can be gained by simply looking at cluster-snapshots of the simulation (see figure 1). All hydrogen bonded molecules are shown in the picture. If a O–H(DMSO) distance is shorter than 2.5 Å the oxygen donating molecule is also depicted. If necessary the important DMSO is marked with an arrow. Most often the DMSOs

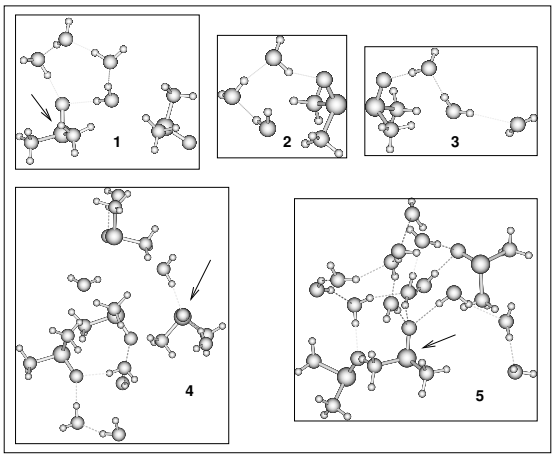

Figure 1. Clusters from the Car–Parrinello simulation.

are involved in a very expanded hydrogen bond network, e.g. cluster 4 and 5 in figure 1. This is in accordance with [8], where the authors found indications for a more complex hydrogen bond

network. The question of how far it can reach stays open for the investigation of a bigger system. We observe a coordination number of three around the DMSO-oxygen from time to time (example in the fifth cluster figure 1). Furthermore methyl group contacts, i.e close distances between the DMSO hydrogens and hydrogen acceptors are seen very often, for instance all clusters of figure 1. "Rüssel"-structures [10] (cluster 2 and 3) are seen very often, i.e. when a chain of hydrogen bonded water molecules forms a trunk like structure starting from the DMSO oxygen ending at the methyl groups. 1-DMSO–3-H_2O unities could not be confirmed by traditional molecular dynamics simulations, but they appear in the Car–Parrinello simulation (cluster 2 and 3).

4. Radial pair distribution function

Further understanding is provided by the radial pair distribution function in figure 2. For each picture the *solid line* gives the hydrogen-acceptor–hydrogen function and the *dashed dotted line* shows the hydrogen–hydrogen function (all intramolecular contributions are omitted). The hydrogen in (**A**) is from the H_2 molecule (dissolved in ammonia), in (**B**) it is from the water and in (**C**) it is from the DMSO methyl groups.

Thus, in (**A**) of figure 2 two functions of a H_2 molecule prepared in situ in ammonia, i.e. a hydrophobic system, [20] are shown. In this system the hydrogen atoms from the ammonia molecules reach closer distances to the H_2 than the nitrogen atoms (i.e. the hydrogen acceptor atoms). The function is in agreement with the function for argon in water, as it exhibits the characteristic shoulder. This shoulder indicates the coupling functionality between the first and second water shell of the hydrogen atoms around the apolar particle [21].

Graph (**B**) simply shows the function for water from our system. The *solid line* displays the well-known feature: a pronounced hydrogen bond peak at approximately 2.0 Å and the second neighbor shell at 3.7 Å. This agrees well with the pure water Car–Parrinello simulation of a 32 water system [22] (peaks at 1.8 Å and 3.4 Å). Whereas the almost equal height of both peaks

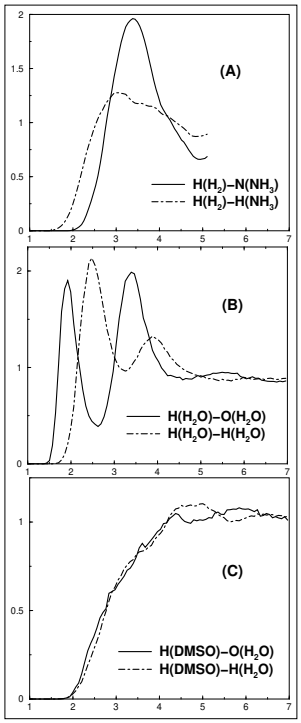

Figure 2. Radial pair distribution functions from H_2 in NH_3, H_2O, and DMSO/H_2O simulations.

is partially due to the small box (in the 64-Car–Parrinello water the first peak is lower than the second) and partially due to the influence of the DMSO, the shift of the first peak (2.0 Å instead of 1.8 Å) is not an artefact of the small box. Both are effects due to the DMSO molecules as observed in the traditional molecular dynamics simulation with the FS-model [9]. (Note, that the FS-model is the most reliable model as it does not use the united atom ansatz and it allows flexible molecules like the model of [23], but it relies also on the pairwise additivity). For the H–H function (*dashed dotted line*) one observes two peaks at location 2.5 and 3.9 Å. In both pure water Car–Parrinello simulations [22,24] the two peaks are at 2.3 and 3.8 Å reflecting the same shift as in the O-H function. This again, is in accordance

with traditional simulation [9].

Comparing these two extreme situations of a hydrophobic and a hydrophilic system, one recognizes that the corresponding functions for the hydrogen atoms of the DMSO molecules rather resembles the hydrophobic case (**A**). Both functions lie on top of each other. The functions are not yet decreased to unity reflecting a too small system. In perfect agreement with the $H(CH_3)$–$H(CH_3)$ function of the experiment and previous simulations from [3], but in contrast to the corresponding $C(CH_3)$–O(H2O) and $C(CH_3)$–$H(H_2O)$ from the simulations of [4], our functions do not exhibit sharp peaks.

5. Orientation

5.1. Angular distribution

In figure 3 the angular distribution of the $H(CH_3)$–$O(H_2O)$ vector with the OH-vector of the water molecule is depicted for different close water molecules. If $\cos\alpha \approx -1$ (α=180°) the hydrogens of the water molecule point away from the methyl groups, and if $\cos\alpha \approx 1$ (α=0°) the hydrogens of the water orients towards the hydrogen atom of the methyl group. The *long dashed line* includes all water if their oxygen is further away than 4.0 Å from the methyl hydrogen, the *dashed-dotted line* shows the orientation if the oxygen atoms are further than 2.7 Å, but closer than 4.0 Å and the *solid line* shows the situation of the water molecules if their oxygens are within a 2.7 Å radius. The inlet gives a closer look for bulk water.

The first impression of the distribution accounting for all water molecules (*dashed line*) indicates no preferential orientation of the water molecules around the methyl group hydrogen atoms. Upon closer inspection (inlet in figure 3), one recognizes a broad distribution between 100° and 40° and the angle of 0° also appears very often, i.e the water-hydrogens are on average pointing towards the methyl-hydrogens. This is in accordance with [19], where a wide distribution of angles and no pronounced preferential orientation towards the carbon atoms was observed. The situation changes accounting for water molecules closer to the methyl group hydrogen atoms: For the 4.0 Å plot there are two peaks at approximately 180° and 80°, i.e here the water are in the well-known tangential orientation. Accounting only for even closer water molecules (2.7 Å), we see a wide distribution around 120°, showing that both hydrogen atoms of the water molecules try to stay furthest from the hydrogen atom of the methyl group. This indicates a near-hydrophilic–far-hydrophobic behavior. It is in agreement with the observation of the weak methyl hydrogen atom–oxygen atom contact [10,25], with the fact that DMSO methyl group is slightly acidic ([1] p.56) and with the prognosis from the Vaismann–Berkowitz [2] simulation. A second distribution of interest is the

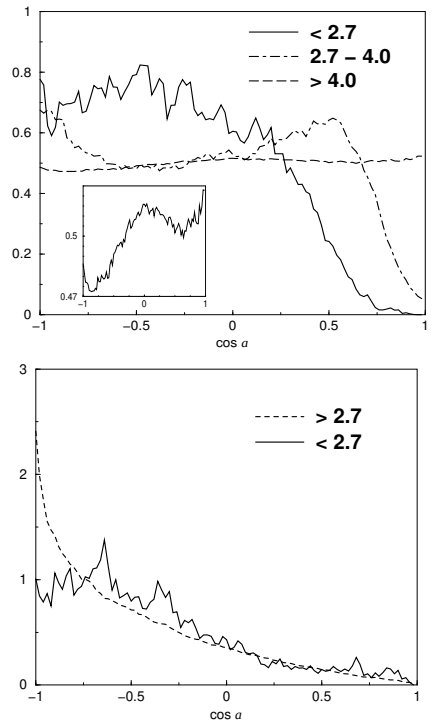

Figure 3. Angular distribution of the OH-vector (upper panel) and the water dipole vector (lower panel) with the $H(CH_3)$–$O(H_2O)$ vector. See text for further explanations.

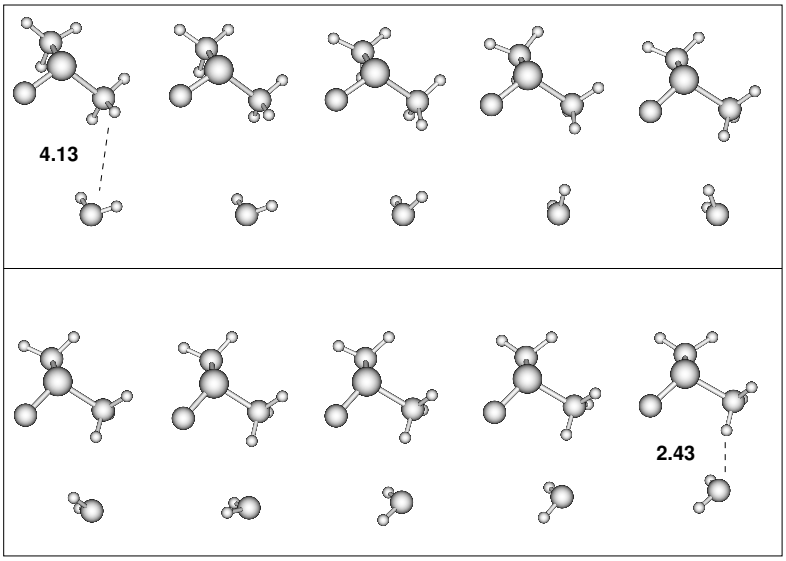

Figure 4. A water molecule approximating the methyl hydrogen atom. First and the last picture display the $O(H_2O)$–$H(CH_3)$ distance in Å.

water dipole moment around the DMSO hydrogen. Figure 3 (lower panel) shows a distribution for the bulk which would be expected for a hydrophobic system. In average both hydrogen atoms are rather pointing to the methyl hydrogen instead of the other way around. Looking at the distribution of the water molecules closer than 2.7 Å, one recognizes the reduction of the high probability of this hydrophobic orientation, again indication a near-hydrophilic–far-hydrophobic interaction, but with a clear dominance of the hydrophobicity.

5.2. Mechanism of near-hydrophilic–far-hydrophobic behavior

Figure 4 displays the evolution of a water molecule approaching the methyl group hydrogen atom (cluster 2 from figure 1).

Between each snapshot 15 fs are passed and all surrounding molecules are cut away. Note, that the water molecule is bonded via one of its hydrogen atoms with two water in a Rüssel-like fashion to the DMSO-oxygen and that -except for the first and the last picture- the water molecule is hydrogen bonded via its oxygen atom to a bulk water, i.e there is one free hydrogen atom. In the first three snapshots the hydrogen atoms of the water point to the methyl hydrogen atom in a tangential orientation. The oxygen accompanied by the free hydrogen of the water moves about 0.10 Å towards the methyl group. The next step is much more rapid (0.40 Å). This is only partly due to the water molecule moving, it is also due to the slight methyl group rotation. Then again such a big step is undertaken by the hydrogen, but the oxygen moves only about 0.15 Å. At this stage, the water adjusts in a 180° $H(CH_3)$-H-O angle and reaches afterwards the minimum distance with its hydrogen atom (last picture of the first row). Finally, a big step of the water oxygen until the water molecule is perpendicular to the C–H axis (see second picture lower row) is followed by slow steps (0.10 Å) to the stage where the oxygen is closer than both hydrogens of the water.

6. Conclusion

In our study, we observed what was indicated in static isolated cluster calculations [10] already: O–H(CH_3) contacts, 1-DMSO–3-H_2O cluster and a coordination number greater than two for the DMSO oxygen. In accordance with the traditional molecular dynamics simulation we see the elongation of the water hydrogen bonds and we find a very involved hydrogen bond network. An interesting feature was reflected in the average orientation of the water at the methyl hydrogen: very close to the methyl group hydrogen atoms the water seem to orient hydrophilic and further away the water molecules are oriented like in a hydrophobic system. The emerging picture of a near-hydrophilic–far-hydrophobic behavior for the methyl groups is based on the static cluster calculations [10], where the attractive nature of the methyl group hydrogen bond could be shown, and on the appearance of these clusters in the present molecular dynamics simulations. In further investigations a statistic analysis of the hydrogen bonds is planed. We hope to be able to make use of the shared electron number (SEN) concept as further developed in the article of [26]. SEN can be related to the hydrogen bond energy between two atoms in a linear fashion. It remains to be tested whether this concept works for structures away from the minimum geometry. Based on this concept one could directly decide whether the C(CH_3)–O(H_2O) interactions are attractive or mainly a product of packing effects. Standard criteria should serve to analyze the life times of the observed clusters in order to test their stability.

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